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STUDIES OF REACTION GEOMETRY IN OXIDATION AND
REDUCTION OF THE ALKALINE SILVER ELECTRODE

THIRD QUARTERLY REPORT

Elliott A. Butler
Angus U. Blackham



February 15, 1969

J. P. L. 952268

Brigham Young University
Provo, Utah

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ABSTRACT

The cyclic current-step (c.c.s.) apparatus has been modified to reduce the direct current signal to less than $\pm 0.2 \mu\text{A}$. Measurements for the ferrous-ferric, $\text{Ag-Ag}(\text{NH}_3)_2^+$, $\text{Ag-Ag}_2\text{O}$ systems and for an equivalent circuit are compared. Measurements of the oxide layer (Ag_2O and AgO) resistance show an increase in the resistance with electrode cycling. The use of oxide layer resistance measurements for further study of the $\text{Ag} \rightarrow \text{Ag}_2\text{O} \rightarrow \text{AgO}$ system is discussed.

Additional data are presented comparing the methods of constant current charging and potentiostatted charging for surface area estimation. Roughness factors of 58 and 81 respectively are reported for these two methods applied to porous sintered silver electrodes. The height of the initial current peak as a function of potential for potentiostatted charging is reported and discussed for smooth silver electrodes.

The effects of ultrasonic vibrations applied during various oxidation steps have been studied. We observed the increase in charge acceptance caused by vibrations to be the same whether the electrode is exposed during the first oxidation plateau, during the second oxidation plateau, or during both oxidations plateaus. Evidence is presented which indicates that no permanent charge acceptance increase results from subjecting electrodes to vibrations during the first cycle only. Tension applied to a silver wire electrode during oxidation did not result in any change in the charge acceptance.

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S E C T I O N I
KINETIC STUDIES OF THE OXIDATION OF SILVER
IN ALKALINE ELECTROLYTE

Introduction

An objective of the experimental work has been the investigation of the possible applicability of the cyclic current-step (c.c.s.) method to the study of the $\text{Ag-Ag}_2\text{O-AgO}$ system. The c.c.s. method has interest because it does not have the limitations of the galvanostatic method caused by the buildup of oxide on the electrode surface.

In a previous report¹ c.c.s. measurements of the $\text{Ag-Ag}_2\text{O}$ system were reported. Although these results had some similarity to those obtained on the ferrous-ferric and $\text{Ag-Ag(NH}_3)_2^+$ systems, some important differences were noted. In this section further c.c.s. studies of this system are reported.

Another objective of the experimental work in this report is the determination of the oxide film resistance as a function of thickness and type of oxide. The drastic changes in the oxide layer resistance, which occur as the reaction changes from $\text{Ag} \rightarrow \text{Ag}_2\text{O}$ to $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ and the changes in the resistance curve which occur with electrode cycling are of particular interest.

Changes which occur in the wave form of the oscilloscope trace (caused by the square wave current which is passed through the cell) during a constant current oxidation are also reported.

Experimental

The apparatus for the c.c.s. system is described in a previous report.⁴ This apparatus was modified by adding a large filter capacitor, a battery with a voltage divider, and a means for checking direct current

flow through the cell (see Figure 1). All of these added components can be readily switched out of the circuit. The capacitor or the battery makes it possible to shift the output of the square wave generator so that the positive signal is equal and opposite in sign to the negative signal. The battery can also be adjusted to decrease the effect of asymmetry to less than $0.2 \mu\text{a}$. The effect of these circuit changes on the c.c.s. measurements of the Ag-Ag₂O system is discussed in the Results section.

For all experiments performed in ammoniacal electrolyte, a silver counter-electrode was used. For all experiments in KOH electrolyte, a platinum foil counter-electrode was used.

A ferrous-ferric solution $1.0 \times 10^{-2} \text{ F}$ in ferrous and ferric sulfate was made by adding the ferrous and ferric sulfate reagents to a $1.0 \text{ F H}_2\text{SO}_4$ solution from which oxygen had been removed by passing nitrogen through it. During the c.c.s. measurements, the cell was kept under a nitrogen atmosphere.

Results

Wijnen and Smith² used the ferrous-ferric system to test the applicability of their c.c.s. (cyclic current step) method. They determined a value of 5.2 ma/cm^2 for i_0 , the exchange current density. With the circuit modifications mentioned above, our values of 4.2 and 4.6 ma/cm^2 for i_0 compare favorably. The graph of $\Delta \eta_0$ versus $1/\omega$ is shown in Figure 2 where $\Delta \eta_0 = [\eta(\theta') - \eta(\theta'')]_{\theta = 0.5}$. From these curves i_0 is calculated with the equation $i_0 = \frac{RT}{nF} \times \frac{1}{\text{intercept}}$

Attention is called to two parts of each curve. The linear part from which the pertinent slope and intercept are determined, is obtained at lower frequencies of the square wave current. At higher frequencies a linear part with a larger slope and a negative

intercept is observed.

The $\text{Ag-Ag(NH}_3)_2^+$ System

In a similar way, data were obtained for the $\text{Ag-Ag(NH}_3)_2^+$ system. The graph of $\Delta\eta_0$ versus $1/f$ is shown in Figure 3. From these curves i_0 is calculated to be $0.21 \pm .06 \text{ ma/cm}^2$.

The shapes of the curves in Figures 2 and 3 are quite similar. The linear part at low frequencies is the part which when extrapolated, gives positive values for the intercept. At low frequencies most of the square wave current which flows during each half cycle is Faradaic. The part consumed in charging the double layer is small. As the frequency is increased, the part of the current which is used to charge the double layer, increases until a break in the curve is noted and the curve drops off rapidly. In this region, a linear extrapolation will give a negative intercept. This is shown by line AB of Figure 3.

The $\text{Ag-Ag}_2\text{O}$ System

A graph of $\Delta\eta_0$ versus $1/f$ for the silver electrode in KOH solution is shown in Figure 4. The data points are taken at the initial part of the $\text{Ag-Ag}_2\text{O}$ oxidation without any net anodic current flowing. This curve does not have a relatively small slope in the low frequency range as did the curves for the ferrous-ferric, and silver-ammonia systems. The steep slope over the low frequency range with its resultant negative slope, does not permit calculation of the exchange current density, i_0 , with the equations of Wijnen and Smith. The shape of the curve in Figure 2 is closely followed by data obtained from an "equivalent circuit" in which the cell is replaced by a capacitor (750 mfd) and a resistor (170 Ω) connected in parallel.

This similarity indicates a large capacitance associated with

the silver electrode as it is initially oxidized. Such a large capacitance overshadows any voltage response to the diffusion of electroactive species or to the electrochemical reaction at the electrode.

Measurements of the Oxide Film Resistance

In a recent report⁴ a method was described for eliminating iR drop from the voltage measurements of the c.c.s. method. The method includes a bridge circuit so that the portion of the oscilloscope trace which is caused by ohmic potential drop in the cell can be balanced out by a variable compensating resistor. Thus the cell resistance can be read directly from the precision helipot which is used as the compensating element in the bridge circuit. To measure the oxide film resistance similar measurements are made during the constant current oxidation and the initial resistance (caused by the solution iR drop) is subtracted from these measurements to give the oxide film resistance.

The results of resistance measurements made on an electrode during the second and fifth successive oxidation (and reduction) cycles, are given in Figure 5B. The cycling did not change the general shape of the resistance curve but the magnitude of the oxide layer resistance did change. This was especially noted during the $Ag_2O \rightarrow AgO$ plateau. A comparison of the maximum resistance values measured during this plateau for a series of five cycles is made below. Our values are compared with those available in the literature.^{5,6,*}

* Leikis and coworkers⁶ did not report measurements of the oxide layer resistance during the $Ag_2O \rightarrow AgO$ plateau. Their values for the $Ag \rightarrow Ag_2O$ plateau are about an order of magnitude greater than ours.

<u>Number of Previous Cycles</u>	<u>Charging time (min).</u>	<u>Resistance Ohm. Cm.²</u>	<u>Source</u>
0	2.34	0.35	Our Work
1	3.29	0.97	Our Work
2	3.96	1.51	Our Work
3	4.32	2.09	Our Work
4	4.58	2.14	Our Work
0	-	0.55	Ref. 5

Some interesting changes occurred in the waveform of the oscilloscope traces caused by the squarewave current. Figure 5A shows the oscilloscope traces observed during a typical charging curve. In addition to the large increase and subsequent decrease in voltages at the time of the shift from the $\text{Ag} \rightarrow \text{Ag}_2\text{O}$ to the $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ plateau, the changes observed in the waveform of the oscilloscope trace indicate a large increase and subsequent decrease in ohmic resistance. The resistance measurements show a 10-50 fold change in the resistance at the beginning of the $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ plateau. Because of the very rapid change, it is difficult to obtain accurate values. It is important to note that the rapid increase in resistance at the end of the $\text{Ag} \rightarrow \text{Ag}_2\text{O}$ plateau is followed by an even more rapid decrease with the onset of the $\text{Ag}_2\text{O} \rightarrow \text{AgO}$ plateau; thus the rapid drop in resistance is probably caused by the presence of very small amounts of AgO. This suggests that small amounts of an impurity could markedly increase or decrease the resistivity of the oxide film and thus have an effect on the charging capacity and characteristics of the silver electrode. The measurement of the changes in oxide film resistance shows promise as a method for studying the effect of such additives.

Future Work

The study of the oxide layer resistance will be continued. The effect of the following variables will be considered:

1. Electrode history (cycling)
2. KOH concentration
3. Electrolyte impurities or additives ($\text{CO}_3^{=}$, O_2 , Ag^+)
4. Electrode additives
5. Magnitude of the charging current

Equivalent circuits will be devised to study the observed changes in oscilloscope trace waveforms.

SECTION II

SURFACE AREA ESTIMATION

Introduction

The magnitude of the charge acceptance of an electrode is directly proportional to the surface area of the electrode if the layer of reaction product is uniform. In our work two sets of experimental conditions have been assumed to give a uniform depth of oxidation for an alkaline silver electrode: (1) constant current charging and (2) potentiostatted charging. A preliminary comparison of surface areas determined under these conditions was presented in our previous report.⁷ For a sintered silver electrode, roughness factors of 63 by constant current charging and 130 by potentiostatted charging were reported. Some additional data showing closer agreement are reported here.

The height of the initial current peak under potentiostatted charging was also examined⁷ for a possible functional relationship to the surface area. Additional data covering a wider range of experimental conditions are presented here.

Experimental

The comparison runs at constant current charging and potentiostatted charging were carried out in a single electrolytic cell. This cell was described in our previous report.⁷ The runs were made at constant temperature using electrolyte solution--all from a single preparation. The sintered electrodes used were soaked in the electrolyte for one-half hour before oxidation. The only change from one run to the next was the change needed in the electronic circuitry in going from a constant current to a potentiostatted oxidation.⁷ The electrolyte used was 0.10N KOH which had been saturated with Ag_2O to prevent dissolution of the oxide film. The runs were made at $20^\circ\text{C.} \pm 0.1^\circ\text{C.}$

The peak height runs were made under the same conditions as were the potentiostatted charging experiments. The current was measured as the potential drop across a 100 ohm standard resistor and was recorded on a Varian G-11A recorder.

Results and Discussions

The results of experiments comparing surface area estimations by constant current charging and by potentiostatted charging are given in Table I. From the constant current data and the assumption that the current densities are equal because the oxidation times are equal, the effective electrolytic surface area of a sintered silver electrode is calculated:

$$a_2 = a_1 \times \frac{i_2}{i_1} = 2.54(\text{cm}^2) \times \frac{4955 \mu\text{amps}}{319 \mu\text{amps}} = 40 \text{ cm}^2$$

The corresponding roughness factor is

$$r. f. = \frac{40 \text{ cm}^2}{0.688 \text{ cm}^2} = 58$$

From the potentiostatted data and the assumption that at equal potentials the charge acceptances per unit area for the standard and sintered electrodes are equal, the effective electrolytic surface area is calculated:

$$a_2 = a_1 \times \frac{q_2}{q_1} = 2.54(\text{cm}^2) \times \frac{6570 \text{ mcoul}}{273 \text{ mcoul}} = 61 \text{ cm}^2$$

The corresponding roughness factor is

$$r. f. = \frac{61 \text{ cm}^2}{0.688 \text{ cm}^2} = 81$$

The values of 58 and 81 for roughness factors of the sintered silver electrode are closer for the two methods than previously reported (63, 130).⁷ The constant current method gives the lower value in each case.

The initial current peak height was first studied for a possible direct functional relationship to the surface area.⁷ It was observed,¹ however, that a porous sintered electrode responded much the same as a nonporous sheet electrode during the initial period that a specific potential was imposed on each. A potential of 0.32 volt was selected for those determinations. The initial response of smooth electrodes to several potentials under potentiostatted conditions has been measured to broaden the base for comparison. These results are presented in Table II and Figure 6. The graph has some of the same features as the graph of charge acceptance versus applied potential for potentiostatted oxidations. This was reported earlier but given here as Figure 7 for comparison. In the low potential range there is a linear increase of current peak height and charge acceptance with increasing potential. Both curves reach a peak value and then decrease somewhat with further increase in potential. At still higher potentials, both the current peak height and charge acceptance increase with increasing potential. This suggests that the structural changes introduced in the initial oxidation of the electrode determine the extent of the charge acceptance as the potentiostatted oxidation proceeds.

Future Work

The study of current peak height as it compares with total charge acceptance will be extended to non porous electrodes of varying roughness and to a model porous electrode. We have not yet prepared a suitable model electrode with uniform parallel pores.⁸ Our effort in this regard will continue.

S E C T I O N I I I
T H E E F F E C T S O F A P P L I E D S T R E S S E S
O N T H E O X I D A T I O N O F S I L V E R

Introduction

In previous reports we have noted that electrodes which were subjected to ultrasonic vibrations during oxidation increased in charge acceptance by 5 to 50 percent.¹ The greatest proportion of this increase occurred in the second oxidation plateau. This report contains the results of experiments in which vibrations were applied during only one of the oxidation plateaus.

It is a general observation that the time required to reduce an electrode at constant current is shorter than the time which had been required to oxidize it at that current. The runs subjected to vibrations show an even shorter reduction time compared to oxidation time.¹ Additional study of this phenomenon is presented in this report.

Other experiments which were conducted to ascertain the permanence of the increase in charge acceptance caused by vibrations are reported.

The study of the effect of other stresses upon the oxidation of silver electrodes has been started and initial data are reported here.

Experimental

The apparatus and techniques used in making charge acceptance determinations of silver electrodes at constant current are discussed in previous reports.^{1,7}

A Macrosonics Corporation Model 250 FF ultrasonic generator with a power output of 80 watts, tuned to a frequency of approximately 800 KHz, was used in the experiments involving ultrasonic vibrations.

We used the flat-bottomed cell with the transducer, cell, electrode, and other apparatus positioned as described in our last report.¹

The electrodes used were punched from 0.004 inch silver foil which was cleaned by scrubbing with abrasive cleanser. Reaction was limited to one side by coating the other side with a clear, colorless acrylic plastic spray. A current density of $620 \mu\text{amps}/\text{cm}^2$ was used to oxidize the 1.29 cm diameter circular discs punched from this foil. The 0.10 N KOH electrolyte was thermostatted to 20.0°C . and was renewed after each run.

Figure 8 shows the apparatus in use to study the effects of tension. Water at 20.0°C . is pumped from a thermostatted bath through the water jacket surrounding the cell. The cell is a cylinder 10 cm. long with an inside diameter of 1.7 cm. At the bottom is a rubber septum, through the center of which passes the wire electrode. In order to position the electrode, the wire is passed through a hole in the center of a plug inserted in the top of the cell. A cylinder of platinum foil 7.2 cm. long with a diameter of 1.6 cm. is fitted into the cell. The end of this sleeve is positioned flush with the bottom of the cell. The level of electrolyte is maintained just at the top of this platinum counter electrode. The plug at the top of the cell contains two capillaries. One extends down to the level of the top of the platinum. This capillary is connected to an aspirator to permit the removal of excess electrolyte, thereby maintaining a reproducible electrolyte level. This level is set at the top of the counter electrode to provide uniform current distribution.⁷ The other capillary extends 0.05 cm. into the electrolyte and is connected by an electrolyte bridge to a calomel reference electrode.

The silver wire electrode passing through the cell is fastened at the top to a supporting beam and at the bottom to a balance pan which

contains weights. The cell is surrounded by a water jacket which is 5 cm. in diameter.

The silver wire electrodes are prepared by scrubbing with abrasive cleanser and then etching in 6 N HNO_3 for 5 to 10 seconds. Inserting the wire from the bottom through the rubber septum caused contamination and passivation of a significant portion of the electrode. Insertion of the wire from the top avoids this contamination. A guide is temporarily placed in the cell to center and support the wire as it is pushed through the rubber septum. The guide is a length of glass capillary tubing encased in a plastic cylinder 1.6 cm. in diameter. See Figure 8.

Results and Conclusions

The Effect of Vibrations on Charge Acceptance

Increased Charge Acceptance

A series of foil electrodes was oxidized to the evolution of oxygen; reduced, and oxidized again. Eleven of these runs were made with no vibrations. Ten were made with vibrations applied during the first plateau of the first oxidation only. Another ten electrodes were cycled with vibrations during the second plateau of the first oxidation only.

Using the runs without vibrations as a standard, the average of the runs with vibrations during the first plateau (c_1) showed an 11% increase in charge acceptance. (See Table III). The second plateau (c_2) also showed an increase of 12%, indicating that the vibrations during c_1 affected the oxidation during c_2 also. The total oxidation time ($c_1 + c_2$) was therefore 12% greater than similar runs without vibrations.

The averages of the runs with vibrations during c_2 showed no significant increase in c_1 (as one would expect), but showed a 12% increase in c_2 . The total oxidation time ($c_1 + c_2$) therefore increased almost 12%.

The small random increases and decreases in total oxidation time seen in the second oxidation cycles are probably insignificant as they are much less than experimental error. Thus it can be seen that there is no permanent increase in charge acceptance found in cycles following exposure to vibrations.

Decrease in Reduction Time

We have observed a decrease in reduction time ($r_1 + r_2$) in cycles exposed to vibrations. Reduction times are typically up to 10% shorter than the preceding oxidation time ($c_1 + c_2$) for runs not subjected to vibrations. For runs exposed to vibrations during the entire oxidation-reduction cycle, decreases of up to 50% have been observed.¹

In our experiments using vibrations during only one step of the oxidation, an average decrease of 2% was observed if vibrations were applied during c_1 (about 1 minute of exposure) and a 3.5% decrease was observed in runs exposed to vibrations during c_2 (about 8 minutes of exposure). The 21% decrease previously reported resulted from cycles exposed to vibrations for 15 to 40 minutes. These data suggest that this decrease is a function of the length of time the electrode was exposed to the vibrations, although wide individual deviations are seen. The decrease may result from loss of active mass through dissolution or flaking or from a lower current efficiency during oxidation than during reduction.

Summary

We conclude from our experiments with ultrasonic vibrations that the charge acceptance of the silver electrode can be increased up to 50% by subjecting the electrodes to vibrations during the first oxidation. This increase can apparently be obtained by exposing the electrode to vibrations during either the first or second oxidation plateaus or both.

It appears, however, that either a loss of active mass or a lowering of the current efficiency during oxidation occurs during this exposure. No evidence was found to indicate that vibrations during the first cycle caused a permanent increase in charge acceptance in subsequent cycles.

The Effect of Tension on Charge Acceptance

Silver wire electrodes were repeatedly cycled by oxidizing to the end of the first oxidation plateau and then reducing. After 66 cycles, no decrease in the diameter of a typical wire electrode could be measured with a micrometer. Inspection of the electrode after oxidation showed that the reacted area of wire was sharply defined by the septum at the bottom and the electrolyte level at the top. The septum did not leak except when the wire was stretched excessively by too much weight.

The roughness factor and plateau length of c_1 increased almost linearly in the runs made to date. The first plateau length (c_1) typically increased a quarter of a minute each cycle. When the electrode was allowed to oxidize to the evolution of oxygen, the next oxidation to c_1 required a considerably longer time than the linear increase would predict. Subsequent cycling (after this unusually long oxidation time) to c_1 would decrease the plateau length so all the time would fall on the predicted line. Thereafter the times would increase normally. Figure 9 demonstrates this observation.

Figures 10 (a), (b), and (c) show the results of runs at three nominal current densities ($400, 800, 1200 \mu\text{amps}/\text{cm}^2$) with and without tension applied. In each figure the circled points represent runs which were subjected to tension. The numbers above these points indicate the number of pounds of weight used. The weights were applied during the entire cycle in each case. Figures 10 (a) and (b) show no significant

effect caused by tension (unless a leveling trend is discerned after the application of tension in Figure 10 (a)).

Figure 10 (c) shows that the upward trend was reversed after 7.3 pounds were applied. This much weight caused noticeable stretching of the wire. At 7.8 pounds applied tension, this stretching (and downward trend) was more pronounced. The diameter of the wire was decreased, the surface area was decreased, and a decrease in charge acceptance was therefore to be expected. The wire broke when 8.5 pounds of tension were applied. Unoxidized silver wire of the same type also broke consistently when 8.5 pounds of tension were applied.

Future Work

More data will be collected on the effect of tension on charge acceptance. In particular the increases which were noted subsequent to oxidizing an electrode to the evolution of oxygen will be studied.

Information on the effect of other stresses such as torsion and compression on the oxidation of silver will be obtained.

Comparison of Surface Area Estimations for Sintered Silver
Electrodes Using Constant Current Versus Potentiostatted Method.

<u>Constant Current</u>				
Electrode Type	Current (μ amps)	Plateau Length (min)	Average Plateau Length (min)	% Dev. (%)
Sintered silver electrode (.688 cm ²)	4955	9.50	9.36 = T ₁	+ - 4
	4955	9.30		
	4955	9.25		
	4955	9.40		
Standard electrode (glass discs 2.54 cm ²)	319	9.00	9.10 = T ₂	+ - 10
	319	9.80		
	319	9.20		
	319	8.75		
<u>Potentiostatted</u>				
Electrode Type	Potential (volts)	Charge Acceptance (mcoul)	Ave. Charge Acceptance (mcoul)	% Dev. (%)
Sintered silver electrode (.688 cm ²)	.3560	6595	6570	+ - 3
	.3560	6550		
	.3560	6570		
	.3560	6575		
Standard electrode (glass discs 2.54 cm ²)	.3560	281	273	+ - 6
	.3560	272		
	.3560	270		
	.3560	269		

Comparison for Sintered Silver Electrode

Constant Current	Constant Potential
Area = 40 cm ²	Area = 61 cm ²
Roughness Factor = 58	Roughness Factor = 81

TABLE II

Current Peak Height Versus Applied Potential for
Runs at Constant Potential

<u>Potential (volts)</u>	<u>Peak Height (ma)</u>	<u>Average Peak Height (ma)</u>	<u>% Dev.</u>
.4400	6.5, 6.7, 6.6	6.6	± 1
.4055	5.6, 6.4, 5.9	5.9	± 5
.3883	4.7, 5.1, 5.1	4.9	± 4
.3596	3.8, 3.9, 3.7	3.8	± 2
.3308	2.5, 2.6, 2.6	2.5	± 3
.3083	2.0, 2.1, 2.2	2.1	± 3
.4745	6.4, 6.8, 6.3	6.5	± 3
.4575	7.0, 7.1, 7.0	7.0	± 0.5
.4748	6.7, 6.5, 6.7	6.6	± 1
.5012	6.2, 6.5, 6.0	6.2	± 3
.5185	6.3, 6.6, 7.0	6.6	± 2
.5580	7.1, 7.4, 6.7	7.1	± 3
.5355	6.8, 6.6, 7.2	6.9	± 4
.6220	8.5, 7.9, 8.0	8.1	± 3
.5935	7.3, 7.9, 7.4	7.5	± 3
.6450	9.6, 9.4, 8.4	9.1	± 6

TABLE III

The Effect of Ultrasonic Vibrations on Charge Acceptance

of Silver Foil Electrodes 1.29 cm. Diameter.

Temperature Controlled to 20.0° C.

Current Density 520 $\mu\text{amps}/\text{cm}^2$.

	Vibrations During c_1			Vibrations During c_2			No Vibrations	
	Ave. Plateau Length (min.)	Standard Deviation	% Increase	Ave. Plateau Length (min.)	Standard Deviation	% Increase	Ave. Plateau Length (min.)	Standard Deviation
c_1	1.08	0.17	11	0.99	0.12	2	0.97	0.16
c_2	8.39	0.85	12	8.32	2.08	12	6.91	1.67
$c_1 + c_2$	9.47	0.82	12	9.31	1.85	12	7.88	1.29
r_1	2.80	0.38	--	2.83	0.55	--	2.39	3.15
r_2	6.51	0.67	--	6.16	1.39	--	5.53	0.99
$r_1 + r_2$	9.31	0.85	--	8.99	1.83	--	7.92	1.69
c_1'	2.97	0.08	6	3.87	0.69	39	2.79	0.35
c_2'	7.93	1.14	2	6.29	1.46	19*	7.80	2.82
$c_1' + c_2'$	10.90	1.40	3	10.16	1.82	4*	10.59	4.72
	$\frac{r_1 + r_2}{c_1 + c_2} \times 100\% = 98.3\%$			$\frac{r_1 + r_2}{c_1 + c_2} \times 100\% = 96.5\%$			$\frac{r_1 + r_2}{c_1 + c_2} \times 100\% = 100.4\%$	

*Decreases

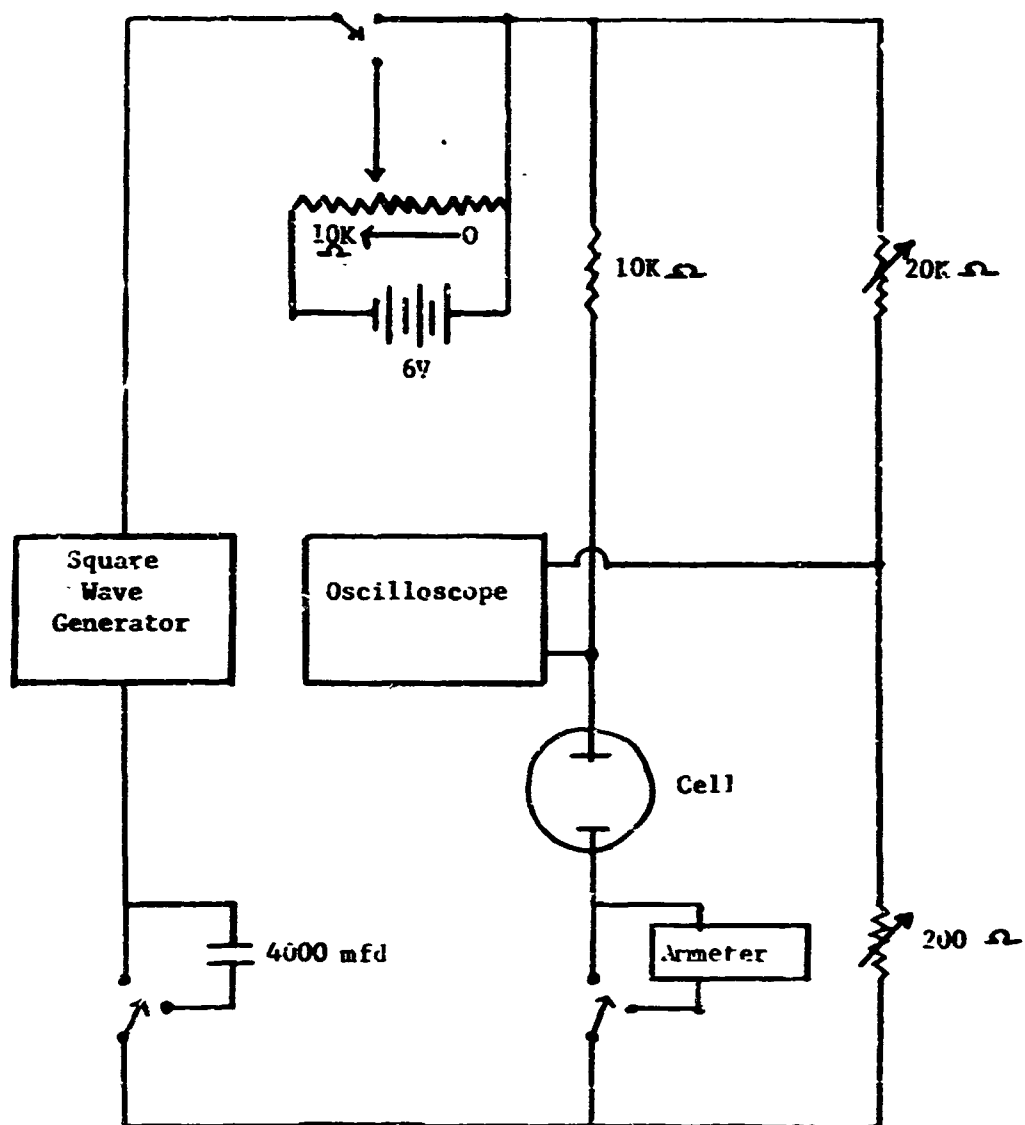


Figure 1. -- Modified C. C. S. Apparatus.

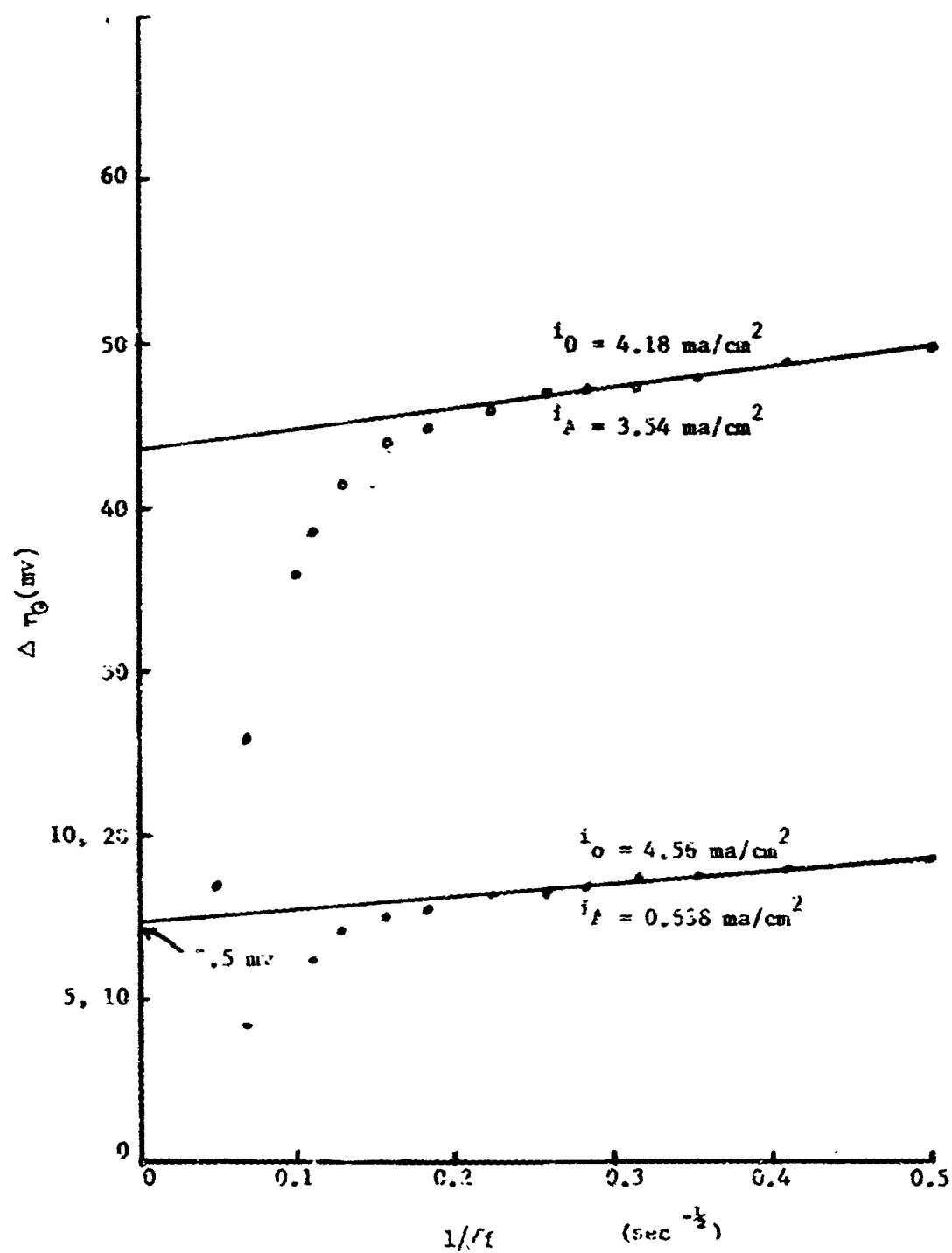


Fig. 2. -- C. C. S. Measurements of the Ferrous-Ferric System

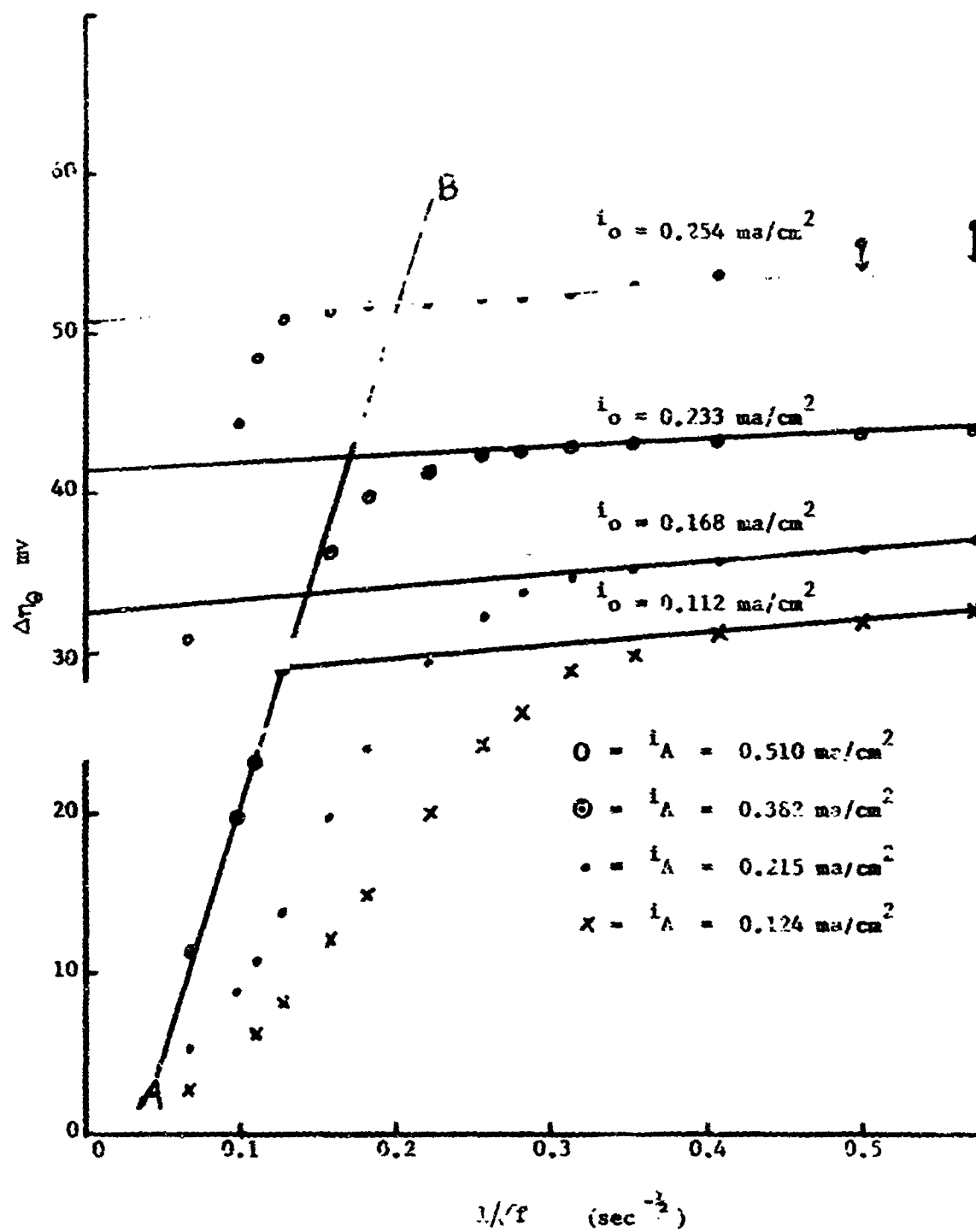


Figure 3. -- C. C. S. Measurements of the $\text{Ag} - \text{Ag}(\text{NH}_3)_2^+$ System

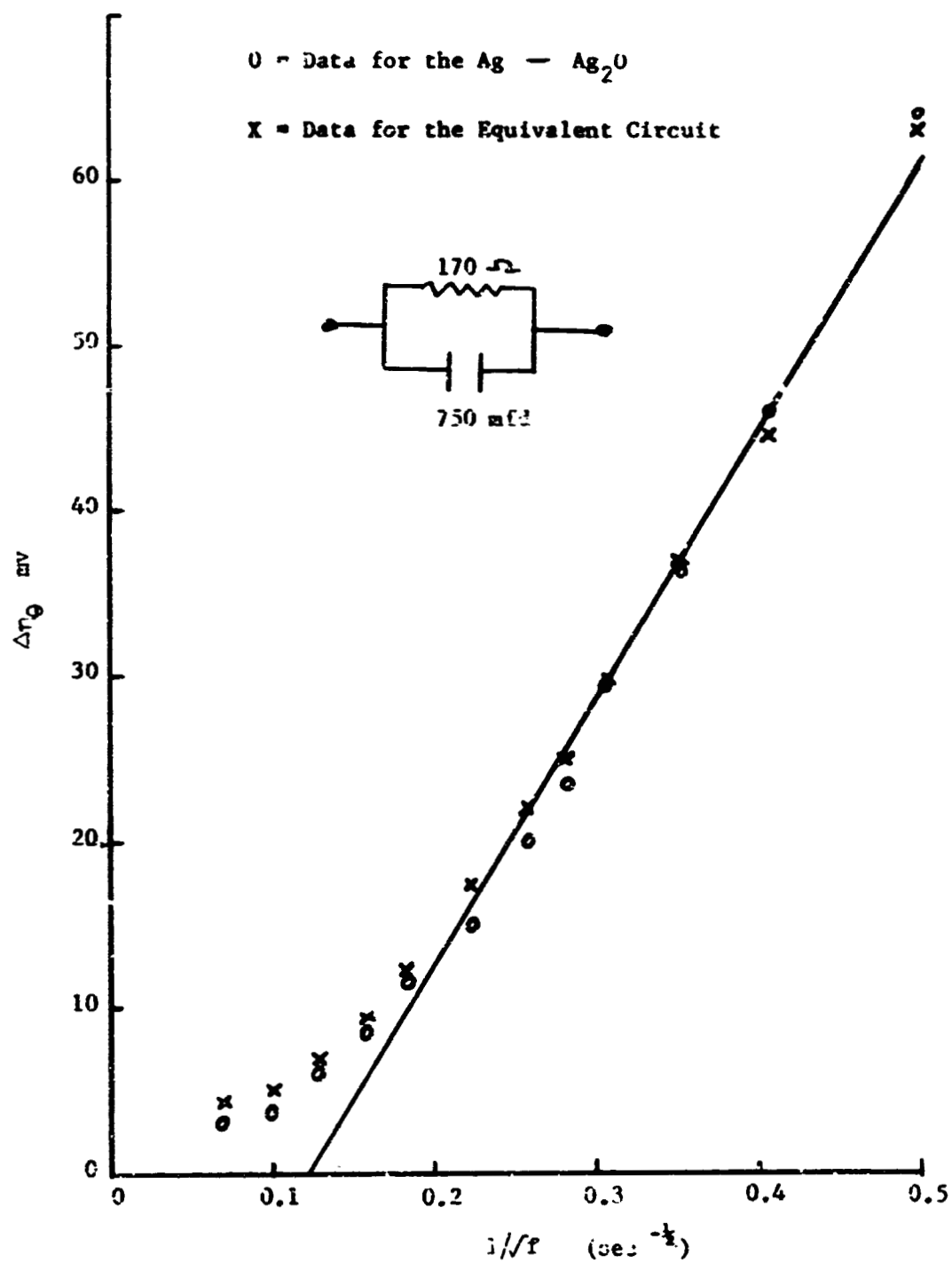


Figure. 4. -- A Comparison of C. C. S. data of the Ag — Ag₂O
 System with C. C. S. data of an equivalent circuit.

Figure 5A

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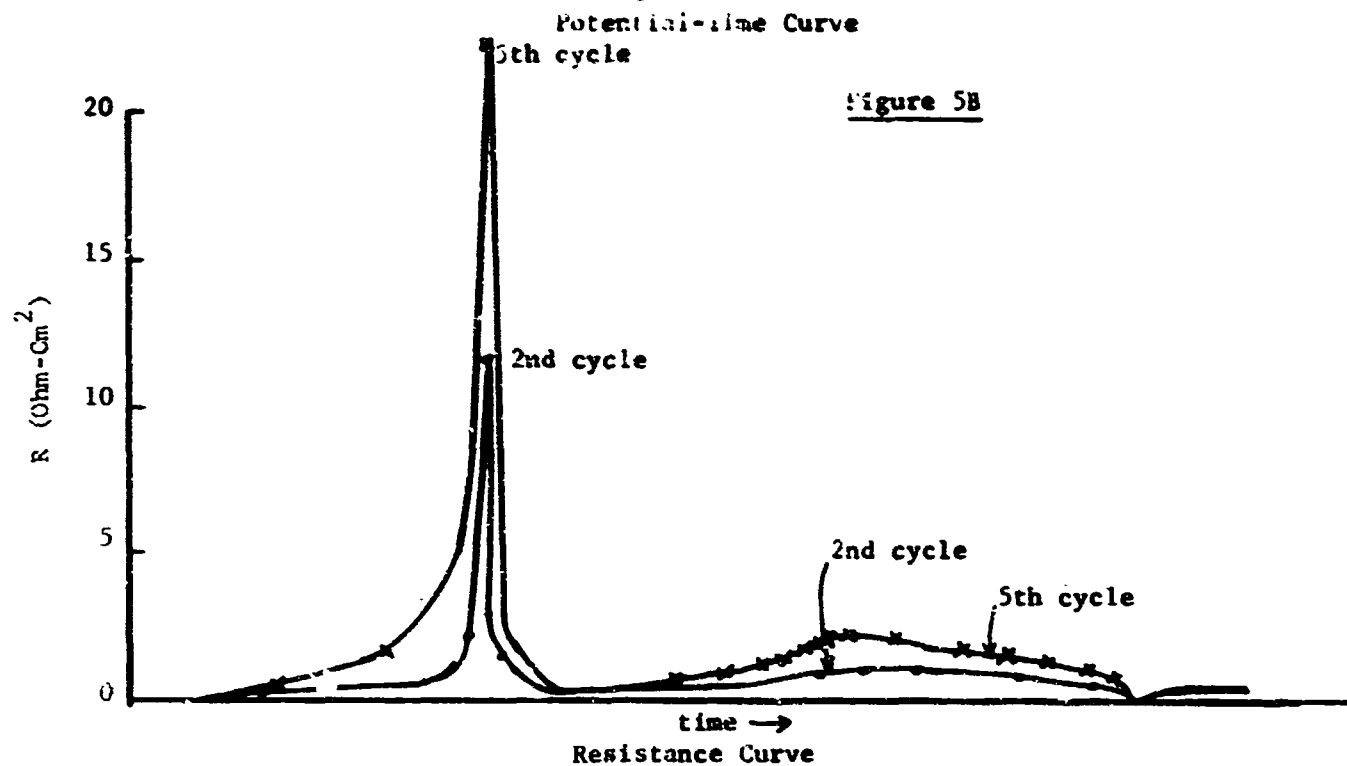
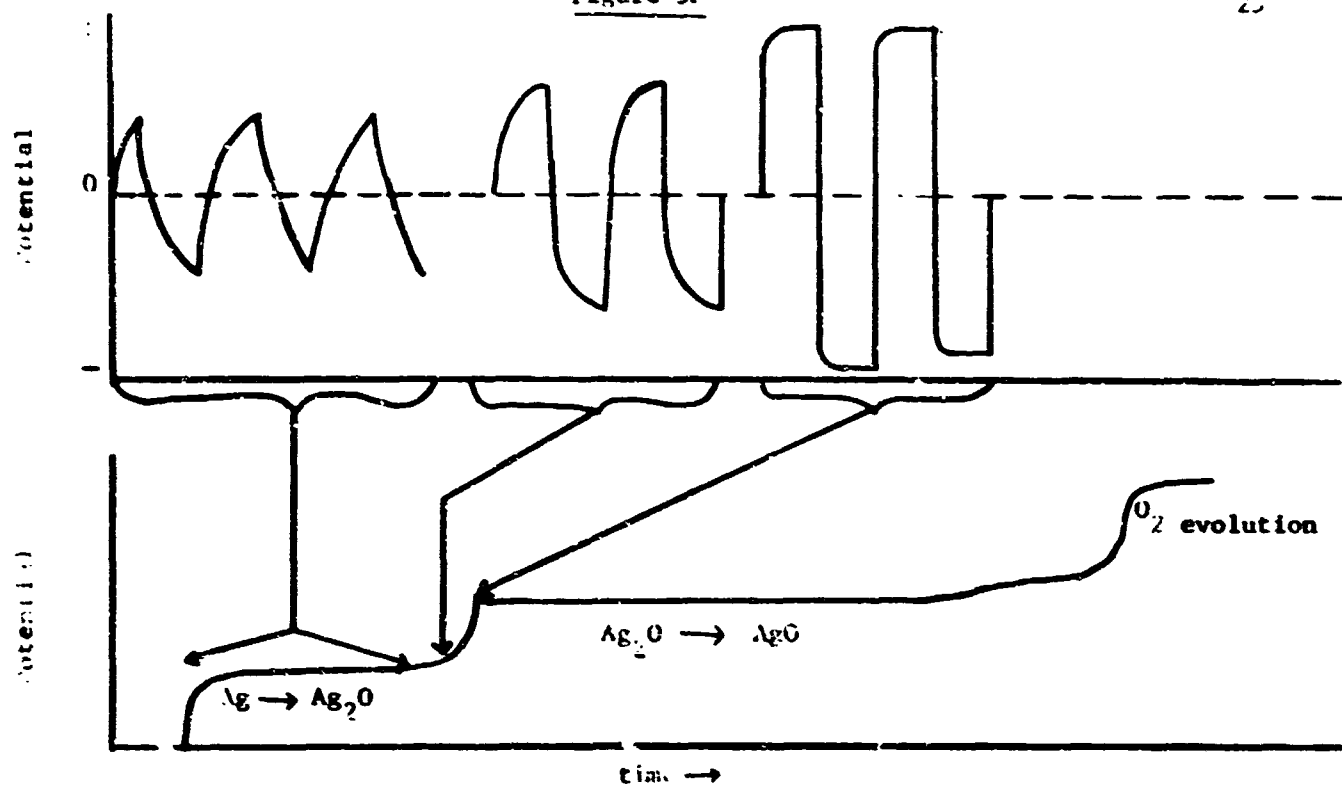


Figure 5A,B -- Comparison of the resistance curve and oscilloscope traces with the potential-time curve. $[\text{KOH}] = 1.09 \text{ F}$.

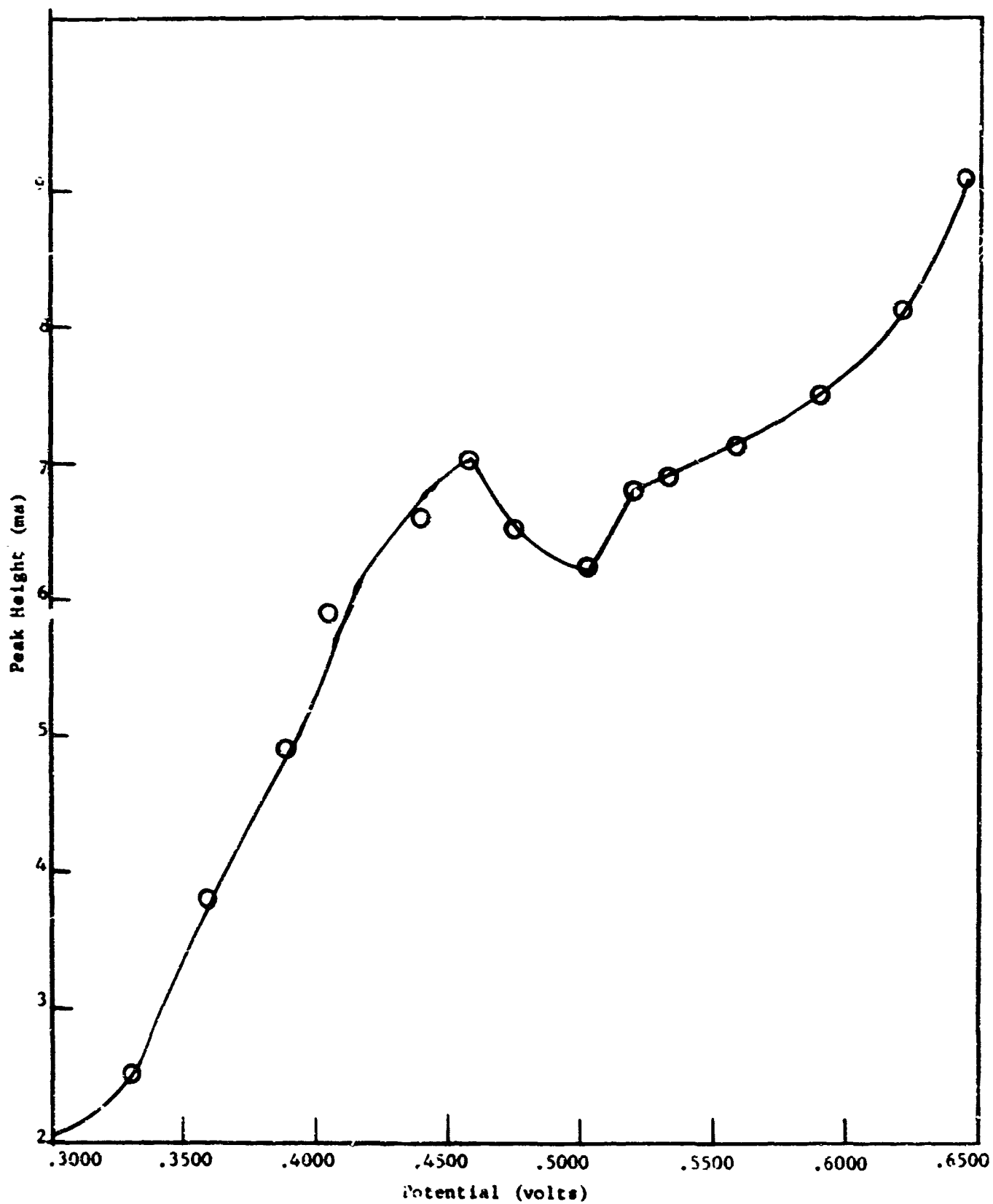


Figure 6. --Peak Height versus applied potential using Hg-HgO reference electrode (ma vs volts).

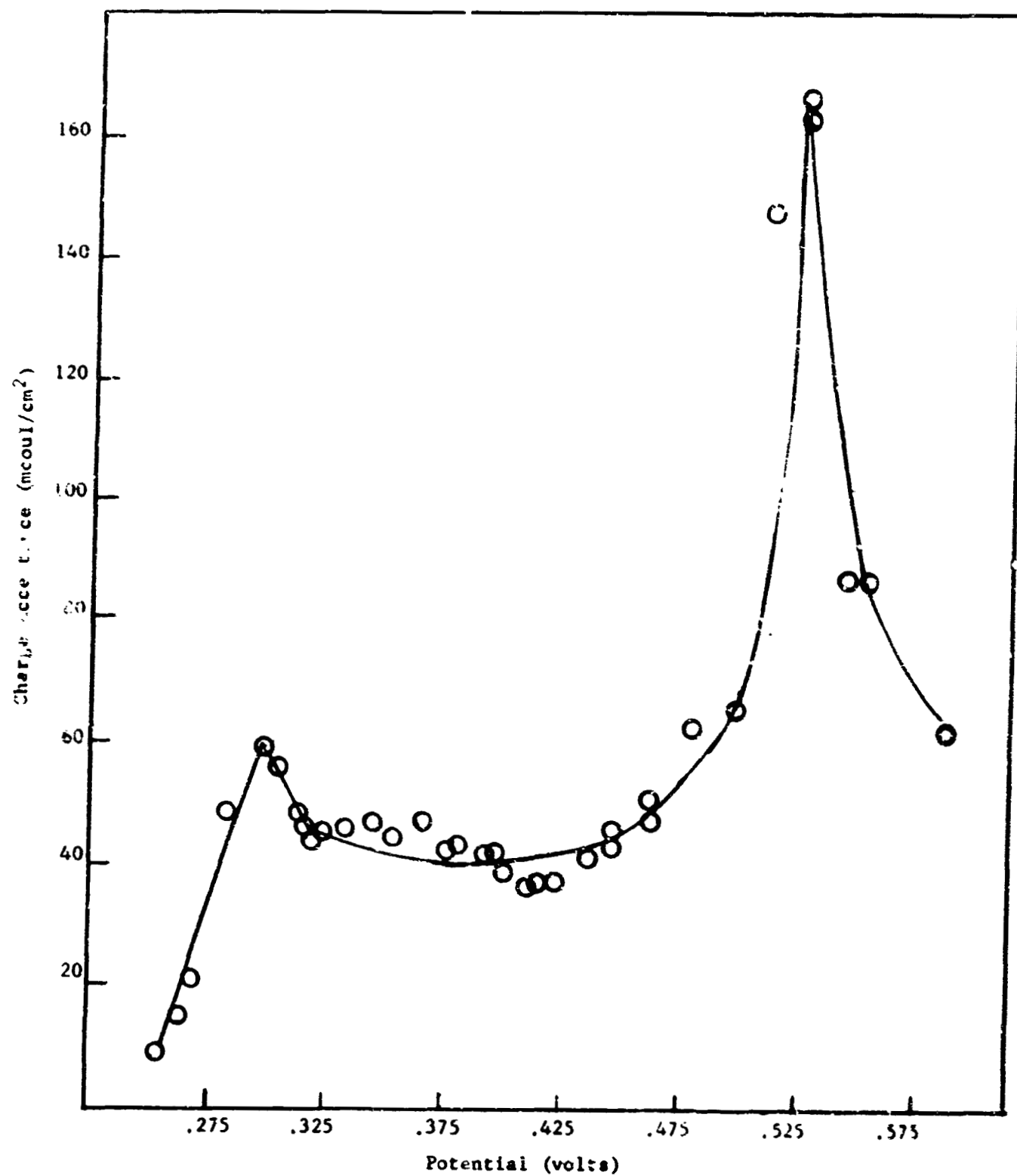


Figure 7. --Charge acceptance per unit area of silver-on-glass electrodes as a function of applied potential.

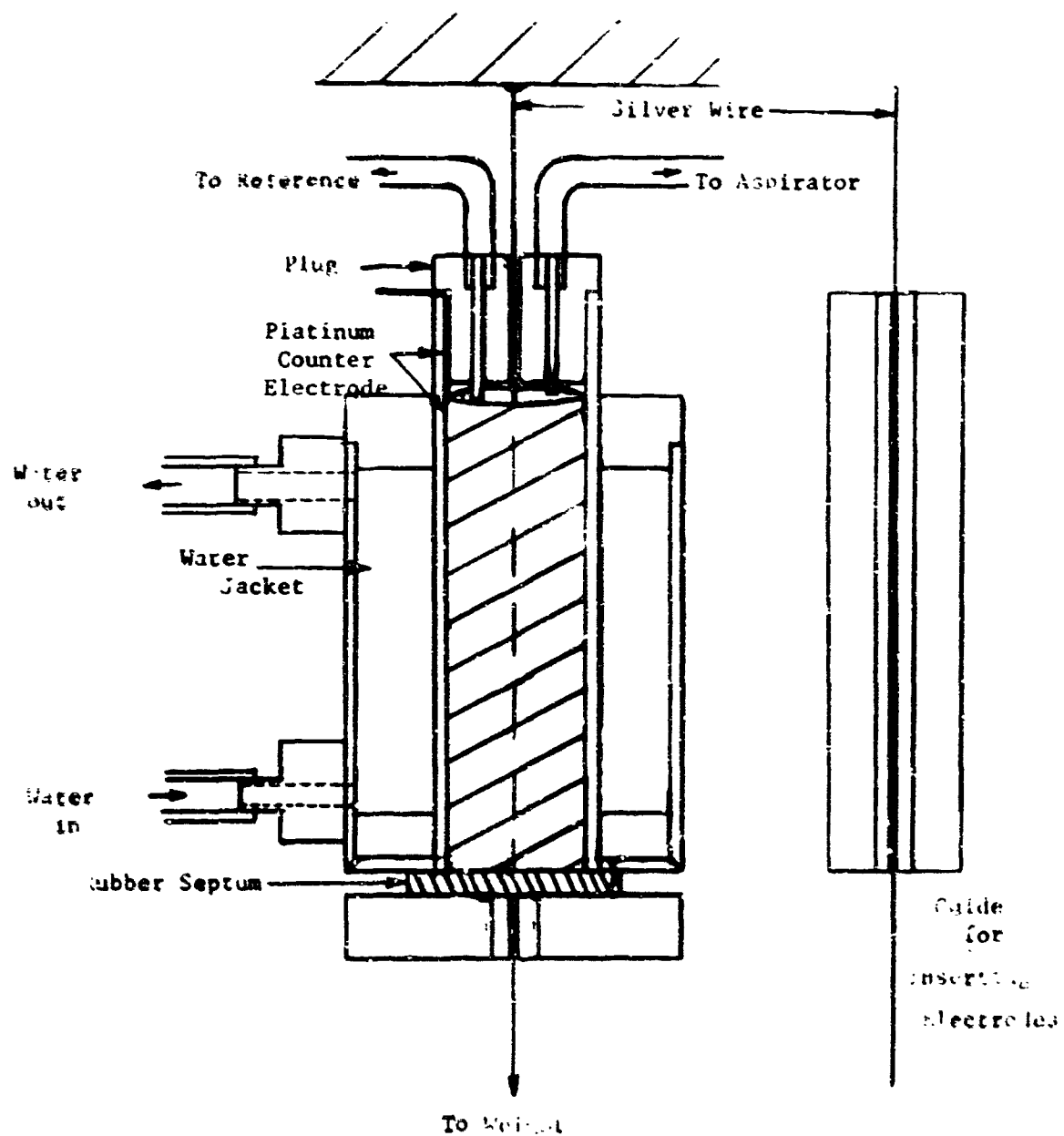


Figure 8. -- the cell used for measuring the effect of tension on charge acceptance.

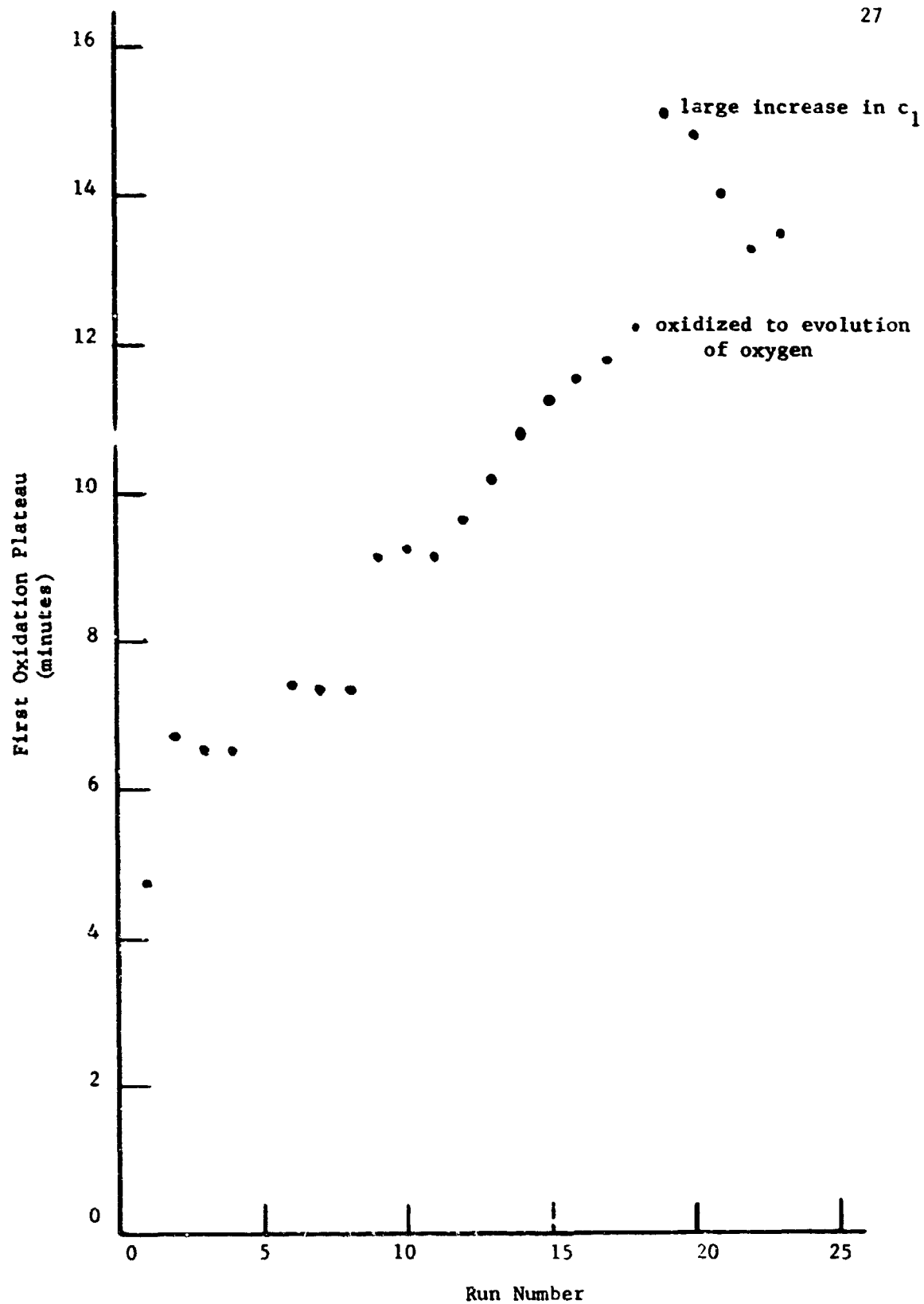


Figure 9. -- A series of oxidation-reduction cycles demonstrating a large increase in plateau length of c_1 immediately following a cycle carried to the evolution of oxygen.

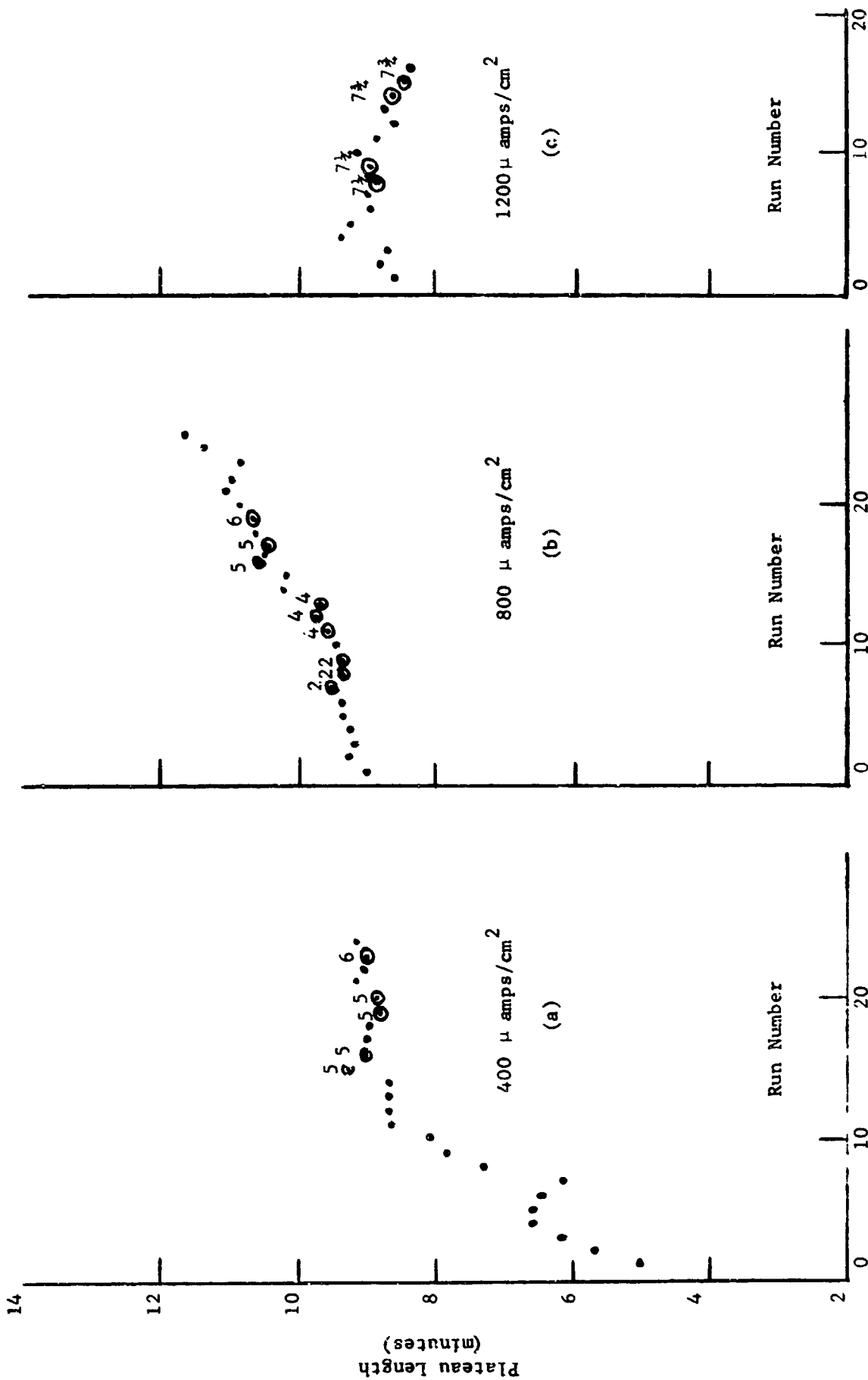


Figure 10. a), b), c).--Silver wire cycled with and without tension. Circled points indicate runs made with tension. Numbers above circled points are total applied weight in pounds. a) shows a leveling trend after application of tension. b) shows no change in linear increase caused by tension. c) shows downward trend when tension sufficient to cause elongation is applied.

REFERENCES

1. E. A. Butler and A. U. Blackham, "Studies of Reaction Geometry in Oxidation and Reduction of the Alkaline Silver Electrode", Second Quarterly Report, J. P. L. 952268, November 15, 1968.
2. M. D. Wijnen and W. M. Smit, Recueil, 79, 289 (1960).
3. M. D. Wijnen and W. M. Smit, Recueil, 79, 22 (1960).
4. E. A. Butler and A. U. Blackham, "Studies of Reaction Geometry in Oxidation and Reduction of the Alkaline Silver Electrode", First Quarterly Report, J. P. L. 952268, August 15, 1968.
5. B. D. Cahan, J. B. Ockerman, R. F. Amlie, and P. Rüttschi, J. Electrochem. Soc., 107, 725 (1960).
6. D. I. Leikis, G. L. Vidovitsch, L. L. Knotz, and B. N. Kabanov, Z. Physik. Chem., Leipzig A, 214, 334 (1960).
7. E. A. Butler and A. U. Blackham, "Studies of Reaction Geometry in Oxidation and Reduction of the Alkaline Silver Electrode", Final Report, J. P. L. 951554, May 15, 1968.
8. R. C. Alkire, E. A. Grens, and C. W. Tobias, Abstract No. 366, The Electrochemical Society, Inc., Fall Meeting, Montreal, Oct. 6-11, 1968, p. 227, 228.